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FUEL CELL SYSTEMS SESSION LOW POWER METHANOL FUEL CELLS, (U)

1976 J PERRY, M KLEIN

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6 FUEL CELL SYSTEMS SESSION

LOW POWER METHANOL FUEL CELLS

(11) 1976

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Methanol has been considered as a reactant in direct air breathing fuel cells because of its high energy content, reactivity, and availability.^{1,2,3} For small size units operating at low power densities, the direct methanol reaction affords advantages of simplicity at attractive fuel utilizations. The chemical reactions of a direct methanol-air fuel cell operating in alkali electrolyte are as follows:



If the alkali electrolyte is not regenerated, it can be considered consumable in the cell reaction and two moles of KOH are required per mole of fuel. For small systems the simplest approach is to manually fuel the power pack with a mixture of methanol contained within the alkali electrolyte. After the methanol is consumed, the unit is drained free of anolyte and can be refilled with a fresh methanol/KOH mixture for use in another discharge.

Figure 1 shows an individual cell and its components. A single cell is made up of two molded polysulfone plastic frames into which two air electrodes are epoxy bonded. The air electrodes are held in place by an internal frame. Centrally located between the two air electrodes are the fuel electrodes which are kept from shorting out against the air

electrodes by the cross ribs of the internal frame. The two outer frames are bonded together to form one cell compartment which is liquid tight. The cell is provided with an O-ring sealed screw and a filling port for the anolyte. A key feature of this concept is the use of an air electrode that will not catalyze the direct reaction of methanol and air since there is no provision for separating methanol from the air electrode. This is accomplished by the use of a silver amalgam catalyst which is virtually inert to direct methanol reaction. The air electrode also contains a micro-porous Teflon backing to prevent electrolyte weeping out the backside of the electrode under the hydrostatic head of the free electrolyte. The air catalyst, loaded at 20 mg/cm², is bonded on a silver expanded metal current collector with Teflon to form a hydrophobic gas diffusion electrode.

The fuel electrodes consist of a silver expanded metal current collector and a catalyst layer, 10 mg/cm², of 30% platinum and 70% palladium. The anode catalyst is bonded together by Teflon, but the electrode is not sintered and is hydrophilic in nature. The methanol reaction is heavily dependent on catalyst quantity and for these first generation units, two back to back fuel electrodes of the type described above were utilized. The anolyte composition is 6 molar methanol-11 molar potassium hydroxide. Based on 100% utilization the fuel mix will deliver 0.96 Ah/cc. Methanol concentrations much above this level may result in wetting and flooding out of the hydrophobic gas diffusion air electrode. Figure 2 shows the voltage current characteristics of a typical single cell which is incorporated into a module.

Utilizing the materials and design concepts described, two different size modules have been fabricated for evaluation. The smaller of the two modules contains two cells in series, mounted in a flashlight as shown in Figure 3. A 10 cc capacity plastic syringe is used to inject 7 cc of fuel mix into the cells. The cells are reactivated by simply removing the fill port screw, shaking the cell module several times to force the spent fuel mix out, and injecting an additional 7 cc of fuel mix. Present draining and refilling procedures are tedious and need improving. The two cell module is designed to operate at 200 to 225 milli-amps (5-6 mA/cm²) at 1.4 volts, and will initially give 15 to 20 hours of service for a capacity output of approximately 3 ampere-hours. Single cells of this type have been refueled and discharged for 20

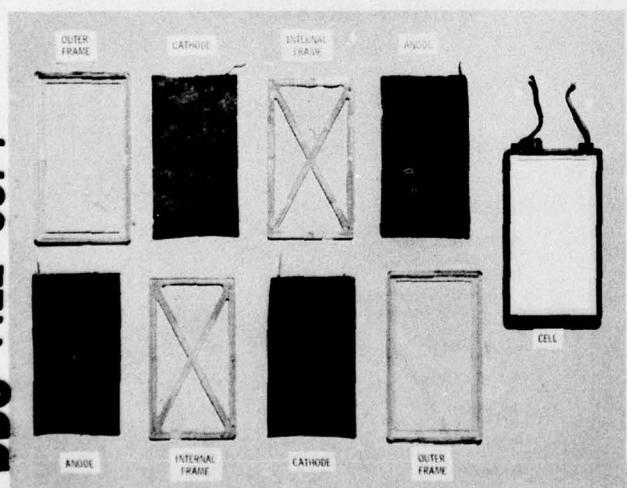


Figure 1. Methanol-Air Fuel Cell and Components.

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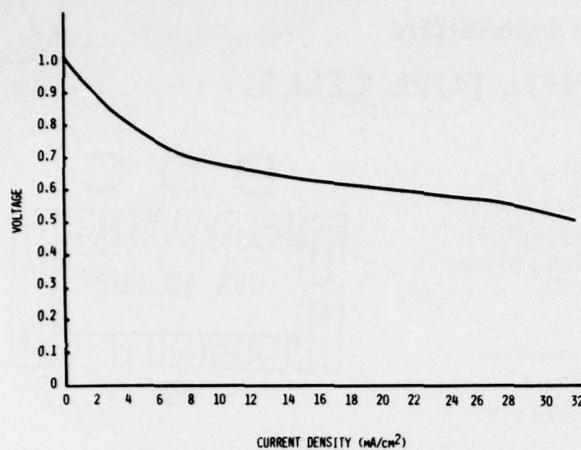


Figure 2. Voltage Current Characteristics of Methanol-Air Fuel Cell.

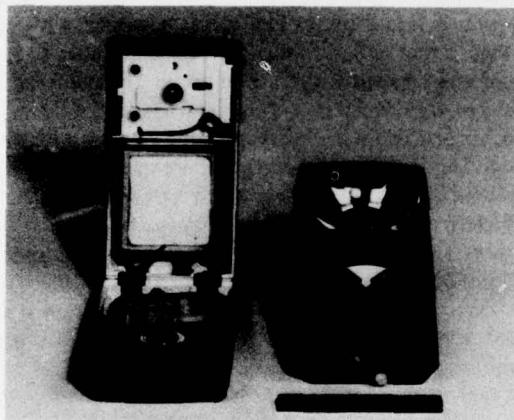


Figure 3. Flashlight Equipped With Methanol-Air Fuel Cells.

times with no change in performance. To evaluate the activated stand retention characteristics of the two cell module in the flashlight, a series of units were subjected to different types of storage at room temperature for various periods of time and then discharged at 200 milliamps. Figure 4 shows the resultant discharge duration versus storage time of a number of two cell modules. Units stored on open shelf for 14 days operated for an hour. This performance decay is attributable to methanol evaporation, which is a function of

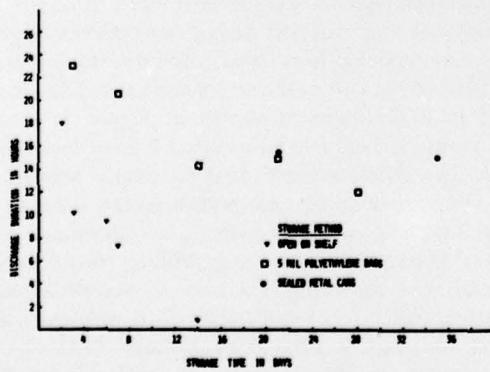


Figure 4. Discharge Duration of the Two Cell Modules After Storage.

the geometry and air ports of the flashlight package. Test results on units stored in a totally sealed metal container showed 15 hours of operation after 35 days of storage, demonstrating a great improvement in charge retention. For those modules packaged in 5 mil polyethylene bags, 50% retention was obtained after 4 weeks of storage. It is envisioned that future modules could be utilized with flashlights that are designed with louvers on the flashlight housing to improve the storage characteristics. Adequate storage methods are required since, aside from methanol evaporation, carbon dioxide in the air has a tendency to form potassium carbonate crystals in the porous Teflon backing of the cathodes that can result in electrode weeping.

The larger module consists of a 6 series-connected cell sized to fit within a conventional 6 V LeClanche lantern battery envelope. This methanol-air battery is shown in Figure 5. Table 1 presents the weight breakdown of the methanol lantern battery.

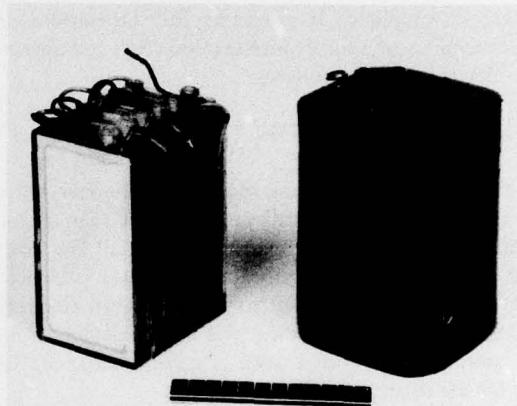


Figure 5. Methanol-Air Lantern Battery.

TABLE 1
METHANOL-AIR LANTERN BATTERY
WEIGHT BREAKDOWN

	<u>GRAMS/CELL</u>
AIR ELECTRODES	6.4
PLASTIC FRAMES	8.6
RETAINING FRAME	5.7
FILLING PORT	0.8
FUEL ELECTRODES	3.9
EPOXY & MISCELLANEOUS	2.1
SINGLE CELL ASSEMBLY	27.5
<hr/>	
	<u>GRAMS</u>
6 CELL ASSEMBLY	165
HOUSING & TERMINALS	61
DRY ASSEMBLY	226
ANOLYTE (17 cc/CELL)	138
WET WEIGHT	364

(0.8 LBS)

Figure 6 shows the discharge performance at 0.5 A (8 mA/cm^2) of the methanol-air battery as compared to a conventional LeClanche lantern battery. The batteries were discharged to a cutoff voltage of 3.6 V. Two performance curves are shown for the methanol-air battery; one shows performance of the battery tested in a lantern case fitted with several small holes and the other curve shows performance of the battery tested open on the bench. The total watt-hours for the methanol-air battery operating in the lantern case is more than 3 times greater than the LeClanche lantern battery tested under the same load condition. The methanol-air battery delivered an energy density of 114.5 watt-hours per kilogram on the initial filling. The battery is capable of a projected energy density of 264 Wh/kg based on 20 recharges of fuel mix.

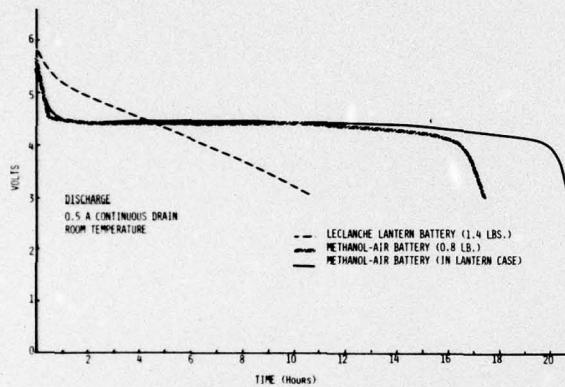


Figure 6. Comparative Performance of Methanol-Air Battery vs LeClanche Lantern Battery.

In summary, the use of a silver amalgam air cathode enables a simplified construction of a direct methanol fuel cell in which a separate anolyte compartment is not necessary. Such units are refuelable for multiple recharges which considerably improve the competitive posture of these modules,

from an energy density standpoint, when compared with other type primary batteries.

Individual cell filling and draining are tedious and future units utilizing a manifold filling port would be simpler to maintain. No particular emphasis was placed on catalyst cost reduction in this work, but to be economically viable, catalyst cost reduction will be necessary that could take the form of low loading catalyst electrodes or non-noble catalysts. Methanol as a fuel is fundamentally limited by its vapor pressure characteristics, and for long periods of storage within active cells, it is necessary to provide some form of louvered air access ports to enable sealing the units when not in use. Air access port sizing is a function of the air supply requirements for a given operating mode and should be optimized for each particular load profile. However, the anolyte can be stored separately in sealed containers for extended periods of time and can be filled into the cells prior to use providing a system of excellent shelf life for short term use.

Due to the lightweight construction and high energy content of methanol, energy densities of approximately 114.5 Wh/kg have been demonstrated. Further improvements in module design (e.g., weight reductions, which permit greater fuel loading for longer discharge durations) would result in improved energy density. The anolyte mix is theoretically capable of 500 Wh/kg at 0.7 volts per cell.

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